Koizumi Laboratory (Special Issue on the Commemoration of the Fortieth Anniversary)

KOIZUMI LABORATORY (January 1962~)

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This laboratory was established for research concerning theory and application of dielectrics in January 1962. The following are individual topics in research which have been done: (1) Static dielectric constant and dielectric relaxation of polar liquids; (2) Dielectric properties of heterogeneous systems: (3) Dielectric properties of insulating materials; (4) Dipole moment and polymer conformation.

I. Static Dielectric Constant and Dielectric Relaxation of Polar Liquids

Polyethylene glycol—Dielectric properties of the oligomer of ethylene glycol were studied over a wide range of frequency by N. Koizumi and T. Hanai. The static dielectric constants of the glycols showed typical dielectric behavior of hydrogen-bonded liquids. In solid state these glycols were almost irrotationally frozen, giving small dielectric constants. Dielectric relaxation of the skewed arc type was observed only for supercooled tetraethylene glycols.

Dielectric relaxation of these glycols in liquid state was investigated at microwave frequencies by N. Koizumi. The value of relaxation time was of the order of 10^{-10} sec at 20°C, being the largest for diethylene glycol and decreasing slightly with higher homologs of this series. This striking feature was discussed in terms of flexibility of the polyoxyethylene chain due to the internal rotation around the C–O bonds of the chain skeleton.

Following the studies on lower-membered polyethylene glycols dielectric measurements were made on polyethylene glycols with molecular weights from 600 to 4000 by N. Koizumi and T. Hanai. In solid state two types of dielectric relaxation occurred: One was due to the relaxation of polar groups and the other was of the wedge type. The latter was ascribed to the space charge polarization of impurity ions. The general feature of a relaxation of the wedge type was discussed. Low temperature measurements indicated the existence of at least two relaxation mechanisms besides the wedge type relaxation. The orientation of hydroxyl groups was responsible for one of them. Although diethylene glycol diethyl ether gave a high dielectric constant associated with the polar nature of the C–O bond in liquid state, no dielectric dispersion was found in solid state.

N-methylamide—Dielectric constants of N-methylamides of acetic, propionic, butyric, valeic, and caproic acids were studied over a wide temperature and a frequency range by N. Koizumi and E. Ikada. Very high static dielectric constants of these compounds were discussed in connection with intermolecular hydrogen-bonding in the liquid state. The temperature dependence of static dielectric constants was fitted precisely with an empirical expression. Dielectric relaxtion studied at vhf region indicated that a single relaxation time due to breaking and reforming of the intermolecular hydrogen bond predominates in the primary dispersion region.

Relatively high values of limiting high frequency dielectric constants in the primary relaxtion of these N-methylamides indicated that another relaxation process would occur at higher frequencies.

Charts of complex function $C\exp(-j\zeta)=[\tanh(T\exp j\tau)]/(T\exp j\tau)$ were prepared to facilitate dielectric measurements on very lossy media at uhf and shf regions, the dissipatation factor to be found by use of the charts ranging from 0.2 to 2.0.

Polyethyleneimine—Dielectric properties of pure liquid polyethyleneimides were studied at frequencies of 10 Hz to 3 MHz. The dielectric constants were relatively low in comparison with those of polyethylene glycols. This suggests that the intermolecular hydrogen bonding is weak and does not greatly contribute to the polarization. The Onsager equation approximately holds between the dielectric constant and the dipole moment for liquid polyethyleneimines. Dielectric relaxation observed in supercooled state showed the overlap of two or more relaxation regions.

II. Dielectric Properties of Heterogeneous Systems

As an continuation of previous work done by T. Hanai, N. Koizumi and R. Gotoh, theories of interfacial polarization for heterogeneous systems have been rigorously discussed for binary and ternary systems of stratified dielectrics and spherical dispersions.

First a general solution of Wagner's theory for a spherical dispersion was derived, and was found to fail in accounting for the experimental results of emulsions at higher concentration. A new theory of the interfacial polarization was developed on the assumption that Wagner's theory holds for an infinitesimally increasing process in concentration of the disperse phase, and led to new expressions for the dielectric constants and the conductivities at high and low frequencies. Concurrently, dielectric constants and conductivities of oil-in-water and water-in-oil emulsions were measured over wide ranges of emulsion-concentration and measuring frequency. The oil-in-water emulsions showed dielectric constants and conductivities which are dependent on the concentration and independent of frequency, and the results were satisfactorily interpreted by the new theory. The water-in-oil emulsions showed an agitation effect on the dielectric properties in addition to a remarkable dielectric dispersion predictable from the new theory. This effect is supposed to be attributed either to the agglomeration of dispersed particles or to the formation of molecular films of detergent at oil-water interfaces, the confirmative study being in progress. According to the new theory, the dielectric dispersion may be observed also in emulsions of oil-in-water type if the dielectric constant of the oil phase is much larger. Such an example of the dielectric dispersion was found in nitrobenzene-in-water emulsions.

As the application of theoretical results for stratified dielectrics, T. Hanai, during his study at University of Cambridge in collaboration with Dr. Haydon et al., investigated the dielectric behavior of a system of lecithin bimolecular films in aqueous solution, and succeeded in evaluating thickness of the films.

From the point of view of interfacial polarization for a ternary system, a particular

interest is taken in lower frequency characteristics, which are being measured accurately by means of both lower frequency bridge method and transient measurements. Effect of D.C. bias voltage on physical properties of the films are also being investigated.

III. Dielectric Properties of Insulating Materials

Precision measurements of dielectric properties of polytetrafluoroethylene (PTFE) and copolymers of tetrafluoroethylene and hexafluoropropylene were made over a temperature range of -40 to $+180$°C at frequencies from 10 Hz to 300 kHz by N. Koizumi, S. Yano, and F. Tsuji. PTFE showed typical dielectric behavior of a non-polar polymer. The loss tangent was about 2×10^{-5}, being almost independent of frequency and temperature. Variation of dielectric constant with temperature in copolymers showed the existence of a trasition point around 60°C. The copolymer with a higher hexafluoropropylene content gave the higher dielectric constant and the higher slope of the dielectric constant-temperature curve. Two dielectric loss peaks were observed for copolymers at about -30 and $+100$°C corresponding to γ and α relaxations respectively. The magnitude of loss peaks increased with increasing hexafluoropropylene content. The origin of these loss peaks was attributed to slightly polar nature of the copolymer chain which resulted from the perfluoromethyl side group. The dielectric constant of copolymers was discussed concerning the side group content. Activation parameters for the dielectric relaxation in copolymers were obtained from the temperature dependence of the loss peak. Values of activation enthalpy and entropy were 80 kcal/mole and 180 e.u. for the α relaxation and 12 kcal/mole and 15 e.u. for the γ relaxation respectively. The α relaxation would be associated with the molecular motion of large segments and the γ relaxation was ascribed to the motion of short segments at or near the ends of molecular chain. Effects of gamma-irradiation on the dielectric properties are being studied.

IV. Dipole Moment

An apparatus for precision measurements of dipole moment was designed using the heterodyne beat method By N. Koizumi, F. Tsuji and H. Okamoto. Excellent stability of the variable frequency oscillator was obtained by use of an oscillator of the Franklin type. Since the output signals of the fixed and variable frequency oscillators were pure sine waves, no spurious zero beat took place in capacitance measurements. The precision in capacitance measurements was about 1 part in 50000.

Dipole moments of the oligomer of ethylenediamine were measured in benzene solutions. The observed dipole moments were in good agreement with those calculated on the assumption of free rotation around the C–C and C–N bonds. Dipole moments of polytetrahydrofurane are being studied in connection with the conformation of molecular chain in solution.

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